

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE
REQUEST FOR FILING NATIONAL PHASE OF
PCT APPLICATION UNDER 35 U.S.C. 371 AND 37 CFR 1.494 OR 1.495To: Hon. Commissioner of Patents
Washington, D.C. 20231

00909

TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)Atty Dkt: P 282646 /EUR 50727/USw
M# /Client Ref.

From: Pillsbury Winthrop LLP, IP Group:

Date: July 23, 2001

This is a **REQUEST** for **FILING** a PCT/USA National Phase Application based on:

1. International Application PCT/EP00/00034 ↑ country code	2. International Filing Date 05 January 2000 Day MONTH Year	3. Earliest Priority Date Claimed 27 January 1999 Day MONTH Year (use item 2 if no earlier priority)
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4. Measured from the earliest priority date in item 3, this PCT/USA National Phase Application Request is being filed within:

(a) ☐ 20 months from above item 3 date (b) ☒ 30 months from above item 3 date,

(c) Therefore, the due date (unextendable) is July 27, 2001

5. Title of Invention MOISTURE-ACTIVATED ADHESIVE COMPOSITIONS6. Inventor(s) Steve B. BURNS
Christopher PHANOPOULOS
Christel VAN DEN BOSCH
Paul D. COLEMAN, Jr.

Applicant herewith submits the following under 35 U.S.C. 371 to effect filing:

7. ☒ Please immediately start national examination procedures (35 U.S.C. 371 (f)).
8. ☒ **A copy of the International Application** as filed (35 U.S.C. 371(c)(2)) is transmitted herewith (file if in English but, if in foreign language, file only if not transmitted to PTO by the International Bureau) including:
- a. ☐ Request;
- b. ☒ Abstract;
- c. 16 pgs. Spec. and Claims;
- d. ___ sheet(s) Drawing which are ☐ informal ☐ formal of size ☐ A4 ☐ 11"
9. ☒ **A copy of the International Application has been transmitted by the International Bureau.**
10. **A translation of the International Application** into English (35 U.S.C. 371(c)(2))
- a. ☐ is transmitted herewith including: (1) ☐ Request; (2) ☐ Abstract;
- (3) ___ pgs. Spec. and Claims;
- (4) ___ sheet(s) Drawing which are:
- ☐ informal ☐ formal of size ☐ A4 ☐ 11"
- b. ☒ is not required, as the application was filed in English.
- c. ☐ is not herewith, but will be filed when required by the forthcoming PTO Missing Requirements Notice per Rule 494(c) if box 4(a) is X'd or Rule 495(c) if box 4(b) is X'd.
- d. ☐ Translation verification attached (not required now).

RE: USA National Phase Filing of PCT /EP00/00034

JC17 Rec'd PCT/PTO 23 JUL 2001

11. ☒ Please see the attached Preliminary Amendment
12. ☐ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)), i.e., before 18th month from first priority date above in item 3, are transmitted herewith (file only if in English) including:
13. ☒ PCT Article 19 claim amendments (if any) have been transmitted by the International Bureau
14. ☐ Translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)), i.e., of claim amendments made before 18th month, is attached (required by 20th month from the date in item 3 if box 4(a) above is X'd, or 30th month if box 4(b) is X'd, or else amendments will be considered canceled).
15. **A declaration of the inventor** (35 U.S.C. 371(c)(4))
 a. ☐ is submitted herewith ☐ Original ☐ Facsimile/Copy
 b. ☒ is not herewith, but will be filed when required by the forthcoming PTO Missing Requirements Notice per Rule 494(c) if box 4(a) is X'd or Rule 495(c) if box 4(b) is X'd.
16. **An International Search Report (ISR):**
 a. Was prepared by ☒ European Patent Office ☐ Japanese Patent Office ☐ Other
 b. ☒ has been transmitted by the international Bureau to PTO.
 c. ☐ copy herewith (___ pg(s).) ☐ plus Annex of family members (___ pg(s).).
17. **International Preliminary Examination Report (IPER):**
 a. ☒ has been transmitted (if this letter is filed after 28 months from date in item 3) in English by the International Bureau with Annexes (if any) in original language.
 b. ☐ copy herewith in English.
 c.1 ☐ IPER Annex(es) in original language ("Annexes" are amendments made to claims/spec/drawings during Examination) including attached amended:
 c.2 ☐ Specification/claim pages #___ claims #
 Dwg Sheets #
 d. ☐ Translation of Annex(es) to IPER (required by 30th month due date, or else annexed amendments will be considered canceled).
18. **Information Disclosure Statement** including:
 a. ☒ Attached Form PTO-1449 listing documents
 b. ☒ Attached copies of documents listed on Form PTO-1449
 c. ☒ A concise explanation of relevance of ISR references is given in the ISR.
19. ☐ **Assignment** document and Cover Sheet for recording are attached. Please mail the recorded assignment document back to the person whose signature, name and address appear at the end of this letter.
20. ☐ Copy of Power to IA agent.
21. ☐ **Drawings** (complete only if 8d or 10a(4) not completed): ___ sheet(s) per set: ☐ 1 set informal; ☐ Formal of size ☐ A4 ☐ 11"
22. Small Entity Status ☒ is **Not** claimed ☐ is claimed (pre-filing confirmation required)
 22(a) ___ (No.) Small Entity Statement(s) enclosed (since 9/8/00 Small Entity Statements(s) not essential to make claim)
23. **Priority** is hereby claimed under 35 U.S.C. 119/365 based on the priority claim and the certified copy, both filed in the International Application during the international stage based on the filing in (country) US of:
- | | <u>Application No.</u> | <u>Filing Date</u> | | <u>Application No.</u> | <u>Filing Date</u> |
|-----|------------------------|--------------------|-----|------------------------|--------------------|
| (1) | 60/117,417 | 27 January 1999 | (2) | _____ | _____ |
| (3) | _____ | _____ | (4) | _____ | _____ |
| (5) | _____ | _____ | (6) | _____ | _____ |
- a. ☒ See Form PCT/IB/304 sent to US/DO with copy of priority documents. If copy has not been received, please proceed promptly to obtain same from the IB.
- b. ☐ Copy of Form PCT/IB/304 attached.

RE: USA National Phase Filing of PCT/EP00/00034

24. Attached:

25. Per Item 17.c2, **cancel original** pages #__, claims #__, Drawing Sheets #26. **Calculation of the U.S. National Fee (35 U.S.C. 371 (c)(1)) and other fees is as follows:**
Based on amended claim(s) per above item(s) ☐ 12, ☐ 14, ☐ 17, ☐ 25 (date)

Total Effective Claims	17	minus 20 =	0	: \$18/\$9	= \$0	966/967
Independent Claims	1	minus 3 =	0	: \$80/\$40	= \$0	964/965
If any proper (ignore improper) Multiple Dependent claim is present,				: \$270/\$135	+0	968/969

BASIC NATIONAL FEE (37 CFR 1.492(a)(1)-(4)): **→→ BASIC FEE REQUIRED, NOW →→→→**A. If country code letters in item 1 are not "US", "BR", "BB", "TT", "MX", "IL", "Z", "IN" or "ZA"

See item 16 re:

1. Search Report was <u>not</u> prepared by EPO or JPO -----	: \$1000/\$500	960/961
2. Search Report was prepared by EPO or JPO -----	: \$860/\$430 +860	970/971

SKIP B, C, D AND E UNLESS country code letters in item 1 are "US", "BR", "BB", "TT", "MX", "IL", "NZ", "IN" or "ZA"

→ ☒ B. If USPTO did not issue both International Search Report (ISR) and (if box 4(b) above is X'd) the International Examination Report (IPER), ----- : \$1000/\$500 + 960/961

(only) → ☐ C. If USPTO issued ISR but not IPER (or box 4(a) above is X'd), ----- : \$710/\$355 +0 958/959

(one) → ☐ D. If USPTO issued IPER but IPER Sec. V boxes not all 3 YES, ----- : \$690/\$345 +0 956/957

(of) → ☐ E. If international preliminary examination fee was paid to USPTO and Rules 492(a)(4) and 496(b) satisfied (IPER Sec. V all 3 boxes YES for all claims), ----- : \$100/\$50 +0 962/963

(these) → ☐ E. If international preliminary examination fee was paid to USPTO and Rules 492(a)(4) and 496(b) satisfied (IPER Sec. V all 3 boxes YES for all claims), ----- : \$100/\$50 +0 962/963

(4) → ☐ E. If international preliminary examination fee was paid to USPTO and Rules 492(a)(4) and 496(b) satisfied (IPER Sec. V all 3 boxes YES for all claims), ----- : \$100/\$50 +0 962/963

(boxes) → ☐ E. If international preliminary examination fee was paid to USPTO and Rules 492(a)(4) and 496(b) satisfied (IPER Sec. V all 3 boxes YES for all claims), ----- : \$100/\$50 +0 962/963

27. **TOTAL = \$ 860**

28. If Assignment box 19 above is X'd, add Assignment Recording fee of -\$40 +0 (581)

29. Attached is a check to cover the ----- **TOTAL FEES \$ 860**

Our Deposit Account No. 03-3975

Our Order No. 38266 282646

C#

M#



00909

CHARGE STATEMENT: The Commissioner is hereby authorized to charge any fee specifically authorized hereafter, or which should have been filed herewith or concerning any paper filed hereafter, and which may be required under Rules 16-18 and 492 (missing or insufficient fee only) now or hereafter relative to this application and the resulting Official document under Rule 20, or credit any overpayment, to the Account/Order Nos. shown above for which purpose a duplicate copy of this sheet is attached.

This CHARGE STATEMENT does not authorize charge of the issue fee until/unless an issue fee transmittal form is filedPillsbury Winthrop LLP
Intellectual Property Group

By Atty: Paul L. Sharer

Sig:

Reg. No. 36004

Fax: (703) 905-2500
Tel: (703) 905-2180

Atty/Sec: PLS/cdw

NOTE: File in duplicate with 2 postcard receipts (PAT-103) & attachments.

SCANNED, # 2

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re PATENT APPLICATION of:

BURNS

Group Art Unit: TBA

Application No.: TBA

Examiner: TBA

Filed: July 23, 2001

FOR: MOISTURE-ACTIVATED ADHESIVE COMPOSITIONS

* * * * *

July 23, 2001

PRELIMINARY AMENDMENT

Hon. Commissioner of Patents
Washington, D.C. 20231

Sir:

Prior to examination on the merits, please amend the above-identified patent application in the manner set forth below.

IN THE SPECIFICATION:

At the top of the first page, just under the title, insert

--This application is the National Phase of International Application PCT/EP00/00034 filed January 5, 2000 which designated the U.S. and that International Application was published under PCT Article 21(2) in English.--

IN THE CLAIMS:

The claims are amended as follows:

1. (Amended) A moisture-activated adhesive composition comprising the reaction product of:
 - (A) a polyisocyanate selected from (a) a blend of polymeric MDI and pure MDI and (b) an isocyanate terminated prepolymer; and
 - (B) an isocyanate-reactive component comprising at least one aliphatic tertiary

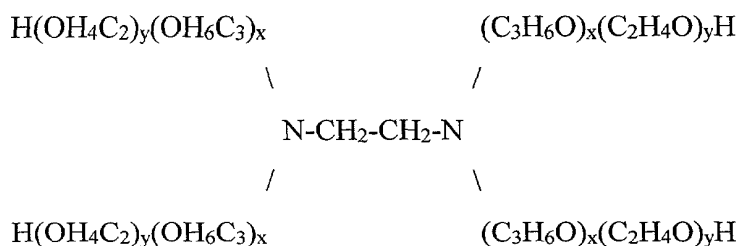
amine group-containing polyol made by alkoxylation of amines or aminoalcohols;

wherein said adhesive composition has a total ethylene oxide content of more than 2.5% relative to the total adhesive composition.

2. (Amended) The moisture-activated adhesive composition according to claim 1, whereby at least 40% of the total ethylene oxide content is present as part of the reactant.
3. (Amended) The moisture-activated adhesive composition according to claim 1, whereby the weight ratio of ethylene oxide to propylene oxide is at least 1 to 8, said propylene oxide being part of the reactant and/or from an additional polyol being present in the composition.
4. (Amended) The moisture-activated adhesive composition according to claim 1, whereby the total nitrogen concentration of the total composition is from 0.002 to 0.05 eqN/100 g.
5. (Amended) The moisture-activated adhesive composition according to claim 1, wherein said polymeric polyisocyanate is a polymeric diphenylmethane diisocyanate.
6. (Amended) The moisture-activated adhesive composition according to claim 1, wherein said composition comprises an isocyanate-terminated prepolymer having an NCO content of 10 to 29%.
7. (Amended) The moisture-activated adhesive composition according to claim 6, wherein said isocyanate-terminated prepolymer is the reaction product of polymeric diphenylmethane diisocyanate and a polyether polyol having a molecular weight of from 1000 to 6000.
8. (Amended) The moisture-activated adhesive composition according to claim 1,

wherein said reactant is an aliphatic tertiary amine group-containing polyol having an ethylene oxide content of 1 to 90%.

9. (Amended) The moisture-activated adhesive composition according to claim 8, wherein said aliphatic tertiary amine group-containing polyol has an ethylene oxide content of 5 to 60%.
10. (Amended) The moisture-activated adhesive composition according to claim 1, wherein said aliphatic tertiary amine group-containing polyol has a molecular weight of 1500 to 10,000 and comprises an initiator having 1 to 18 carbon atoms.
11. (Amended) The moisture-activated adhesive composition according to claim 1, wherein said aliphatic tertiary amine group-containing polyol is prepared from a compound selected from the group consisting of ethylene diamine, triethylene tetramine and triethanolamine.
12. (Amended) The moisture-activated adhesive composition according to claim 11, wherein said aliphatic tertiary amine group-containing polyol is an ethylene diamine-based polyol having the following formula:



wherein x is an integer of 1 to 29.0 and y is an integer of 0.1 to 10.

13. (Amended) The moisture-activated adhesive composition according to claim 1, further comprising a catalyst.

14. (Amended) A process for bonding multiple substrates comprising:
- (1) applying to a surface of a first substrate a moisture-activated adhesive composition as defined in claim 1,
 - (2) contacting said surface with a surface of a second substrate,
 - (3) applying pressure to the contacted surfaces, and
 - (4) curing said adhesive composition.
15. (Amended) The process according to claim 14, wherein at least one said substrate has a moisture content of at least 7% by weight.
- 17.(Amended) The process for bonding according to claim 16, wherein additional moisture is applied to the first substrate surface, the surface of the applied adhesive and/or the surface.

REMARKS

After introduction of the amendment set forth above, claims 1-17 will be pending in the application of which claim 1 is independent. Claims 1-15 and 17 have been amended to eliminate multiple dependency of the claims and to correct grammatical errors. Support for the new claims can be found throughout the original application as filed. *See*, for instance, the claims as originally filed. Applicants submit that no new matter has been introduced by the amendment.

Respectfully submitted,

PILLSBURY WINTHROP, LLP

By: 

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Enclosure: Appendix

APPENDIX

VERSION WITH MARKINGS SHOWING CHANGES MADE

IN THE CLAIMS:

The claims are amended as follows:

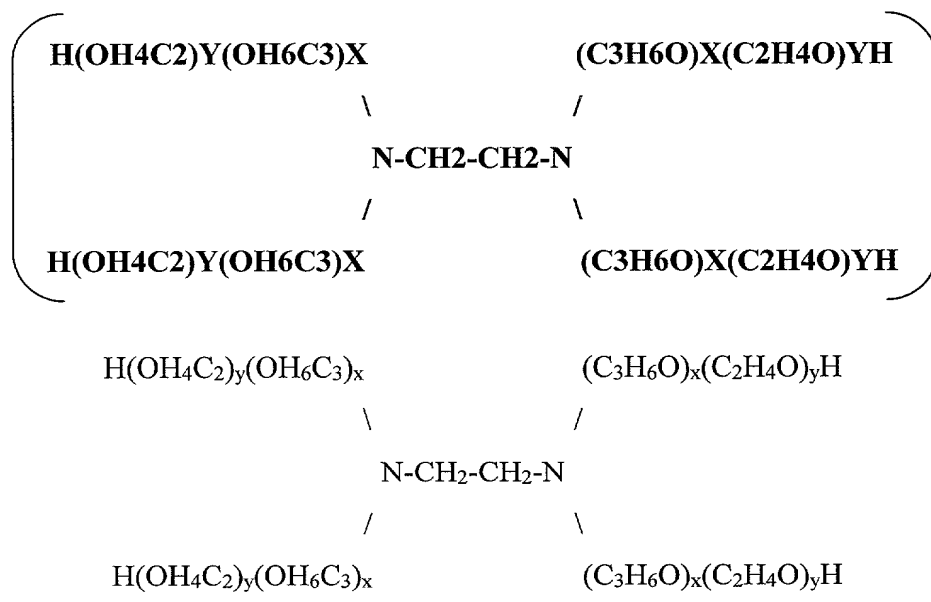
1. (Amended) A moisture-activated adhesive composition comprising the reaction product of:
 - (C) a polyisocyanate selected from (a) a blend of polymeric MDI and pure MDI and[/or from] (b) an isocyanate terminated prepolymer[.]; and
 - (D) an isocyanate-reactive component comprising at least one aliphatic tertiary amine group-containing polyol made by alkoxylation of amines or aminoalcohols;

[characterized in that the total ethylene oxide content by weight of the total adhesive composition is more than 2.5%] wherein said adhesive composition has a total ethylene oxide content of more than 2.5% relative to the total adhesive composition.
2. (Amended) **[A] The** moisture-activated adhesive composition according to claim 1, whereby at least 40% of the total ethylene oxide content is present as part of the reactant.
3. (Amended) **[A] The** moisture-activated adhesive composition according to **[claims 1-2] claim 1**, whereby the weight ratio of ethylene oxide to propylene oxide is at least 1 to 8, said propylene oxide being part of the reactant and/or from an additional polyol being present in the composition.
4. (Amended) **[A] The** moisture-activated adhesive composition according to **[claims 1-3] claim 1**, whereby the total nitrogen concentration of the total composition is from 0.002 to 0.05 eqN/100 g.
5. (Amended) **[A] The** moisture-activated adhesive composition according to **[claims**

1-4] claim 1, wherein said polymeric polyisocyanate is a polymeric diphenylmethane diisocyanate.

6. (Amended) [A] The moisture-activated adhesive composition according to [claims 1-5] claim 1, wherein said composition comprises an isocyanate-terminated prepolymer having an NCO content of 10 to 29%.
7. (Amended) [A] The moisture-activated adhesive composition according to claim 6, wherein said isocyanate-terminated prepolymer is the reaction product of polymeric diphenylmethane diisocyanate and a polyether polyol having a molecular weight of from 1000 to 6000.
8. (Amended) [A] The moisture-activated adhesive composition according to claim 1, wherein said reactant is an aliphatic tertiary amine group-containing polyol having an ethylene oxide content of 1 to 90%.
9. (Amended) [A] The moisture-activated adhesive composition according to claim 8, wherein said aliphatic tertiary amine group-containing polyol has an ethylene oxide content of 5 to 60%.
10. (Amended) [A] The moisture-activated adhesive composition according to claim 1, wherein said aliphatic tertiary amine group-containing polyol has a molecular weight of 1500 to 10,000 and comprises an initiator having 1 to 18 carbon atoms.
11. (Amended) [A] The moisture-activated adhesive composition according to claim 1, wherein said aliphatic tertiary amine group-containing polyol is prepared from a compound selected from the group consisting of ethylene diamine, triethylene tetramine and triethanolamine.

12. (Amended) [A] The moisture-activated adhesive composition according to claim 11, wherein said aliphatic tertiary amine group-containing polyol is an ethylene diamine-based polyol having the following formula:



wherein x is an integer of 1 to 29.0 and y is an integer of 0.1 to 10.

13. (Amended) [A] The moisture-activated adhesive composition according to claim 1, further comprising a catalyst.
14. (Amended) A process for bonding multiple substrates comprising:
- (5) applying to a surface of a first substrate a moisture-activated adhesive composition as defined in **[any one of the preceding claims] claim 1**,
 - (6) contacting said surface with a surface of a second substrate,
 - (7) applying pressure to the contacted surfaces, and
 - (8) curing said adhesive composition.
15. (Amended) [A] The process according to claim 14, wherein at least one said substrate has a moisture content of at least 7% by weight.

17. (Amended) [A] The process for bonding according to claim 16, wherein additional moisture is applied to the first substrate surface, the surface of the applied adhesive and/or the surface.

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re PATENT APPLICATION of

BURNS, et al.

Group Art Unit: not assigned

Appln. No.: not assigned

Examiner: not assigned

Filed: July 23, 2001

FOR: MOISTURE-ACTIVATED ADHESIVE COMPOSITION

July 23, 2001

INFORMATION DISCLOSURE STATEMENT

Hon. Commissioner of Patents
Washington, D.C. 20231

Sir:

Attached is Form PTO-1449 and copies of the references listed thereon. The enclosed references were cited in the also attached International Search Report.

Applicants respectfully request the Examiner to consider each of the documents supplied herewith. It is furthermore respectfully requested that the Examiner confirm the careful consideration in the next official communication by return of an initialed and dated PTO-1449 form in accordance with the provisions of MPEP 609.

This IDS is intended to be in full compliance with the rules, but should the Examiner find any part of its required content to have been omitted, prompt notice to that effect is earnestly solicited, along with additional time under Rule 97(f), to enable Applicant to comply fully.

Respectfully submitted,

PILLSBURY WINTHROP LLP

By



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0989999-10501
T09207 6286886

APPLICATION UNDER UNITED STATES PATENT LAWS

Atty. Dkt. No. PW 282646
(M#)

Invention: **MOISTURE-ACTIVATED ADHESIVE COMPOSITIONS**

Inventor (s): Steve B. BURNS
Christopher PHANOPOULOS
Christel VAN DEN BOSCH
Paul D. COLEMAN, Jr.

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Intellectual Property Group
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This is a:

- ☐ Provisional Application
- ☐ Regular Utility Application
- ☐ Continuing Application
☒ The contents of the parent are incorporated by reference
- ☒ PCT National Phase Application
- ☐ Design Application
- ☐ Reissue Application
- ☐ Plant Application
- ☐ Substitute Specification
Sub. Spec Filed _____
in App. No. _____ / _____
- ☐ Marked up Specification re
Sub. Spec. filed _____
In App. No. _____ / _____

SPECIFICATION

MOISTURE - ACTIVATED ADHESIVE COMPOSITIONSFIELD OF THE INVENTION

The present invention is directed to rapid curing moisture-activated adhesive compositions and methods for their production and a process for bonding multiple substrates using said composition. More specifically, the present invention is directed to specific moisture-activated adhesive compositions which are cold curable in the presence of high moisture content cellulosic or lignocellulosic substrates.

BACKGROUND OF THE INVENTION

In recent years, the use of "engineered lumber" products by the construction industry has become increasingly common - primarily because the availability and cost of adequate quality sawn lumber have become increasingly unfavorable. However, the performance of "engineered lumber" products, which are formed by adhering smaller pieces of wood together into a composite material, represents some major challenges to the adhesives formulator.

Engineered lumber products on the market today, such as finger-jointed lumber, wood I-beams, and glue-laminated beams (glu-lams), utilize a variety of adhesive systems, including phenol - formaldehyde (PF) based adhesives, polyvinylacetate (PVA) adhesives, and isocyanate - based emulsion adhesives. Unfortunately, each of these adhesive systems has limitations, which compromises the effectiveness of the resultant engineered lumber composite.

PF based adhesives require a great deal of heat and time in order to cure, and are sensitive to high levels of moisture in the wood. Use of these adhesives systems requires engineering controls to maintain a low moisture content, and to ensure adequate bonding occurs within the composite. The necessity for such costly catalyst and engineering controls increases production costs, and limits productivity, which in turn limits the competitiveness of engineered lumber in the marketplace. Another major problem associated with these adhesives is their "green strength". These adhesives do not produce adequate bond strength immediately - they typically need to "cure" in order to reach their full potential. This cure time is a matter of hours, often days - which further adds to production costs

PVA adhesives have limited strength. To date, they have not proven to be suitable for use in structural applications, which require physical properties of a certain minimum standard. For example, no commercially available PVA bonded engineered lumber product can meet the ASTM D2259 standard, a frequent requirement for structural lumber applications. Like the PF adhesives discussed above - these systems also suffer from the limitations of slow green strength development, and a dependency on a great deal of heat and time to ensure adequate bond strengths.

Isocyanate-crosslinked latex emulsion adhesives, also have limitations in that these systems also suffer from the limitations of slow green strength development, and a dependency on a great deal of heat to ensure adequate bonding.

Polyisocyanate based adhesive compositions have also been identified for composite wood applications. Examples are moisture curable urethane-modified polyisocyanate adhesives described in EP-B-723 561 which discloses urethane-modified polyisocyanate adhesives for use in plywood panel wood composites. These compositions contain auto catalytic species, designed to increase the reactivity of the polyisocyanate, enabling cure at ambient temperatures in a matter of minutes. However, for engineered lumber products, the different processing requirements between panels and lumber becomes extremely important. As a consequence none of the existing polyisocyanate products, designed for relatively thin composite wood panels, exhibits sufficient reactivity to truly be cost-effective in relatively thick engineered lumber applications.

It is therefore an object of the present invention to provide an adhesive composition especially designed for engineered lumber which impart adequate strength and reactivity and tack without the need for costly catalyst and processing/engineering controls to overcome inherent problems, such as: maintaining low raw material moisture contents, providing a great deal of heat and time in order to cure the adhesive, and protracted "green" strength development.

These objectives are met by the present adhesive compositions, which demonstrate excellent adhesive properties with a prolonged pot life, accelerated cure, particularly at room temperature. Surprisingly, the compositions according to the present invention provide equal performance than those compositions as described in EP 0 723 561. The present compositions are activated by the moisture present in the substrate with which they are being used and thus, they may be most effectively used with substrates having a relatively high moisture content, even as high as 20% or more. Accordingly, the present compositions are effectively used with various types of lignocellulosic materials and are particularly useful in the preparation of engineered lumber products as discussed above.

SUMMARY OF THE INVENTION

The present invention relates to a moisture-activated adhesive composition comprising the reaction product of (A) polyisocyanate selected from either (a) a blend of polymeric MDI and pure MDI and/or from (b) an isocyanate-terminated prepolymer. (B) an isocyanate-reactive component comprising at least one aliphatic tertiary amine group-containing polyol made by alkoxylation of amines or aminoalcohols characterized in that the total ethylene oxide content by weight of the total adhesive composition is more than 2.5%

DETAILED DESCRIPTION OF THE INVENTION

According to the present invention, the polyisocyanate component is selected from either (a) a blend of polymeric MDI and pure MDI and/or (b) an isocyanate-terminated prepolymer. In accordance with the present invention, the blend of polymeric MDI and pure MDI have been found to provide improved penetration into the lignocellulosic substrate and higher wood failure as opposed to glueline failure. A commercially available pure MDI product suitable for use in the present invention is Rubinate™ 44 available from ICI Americas Inc. The preferred blends contain polymeric MDI to pure MDI in ratios of 95:5 to 50:50 and preferably 60:40 to 80:20.

The isocyanate-terminated prepolymers as used herein, the term "isocyanate-terminated prepolymer" includes the prepolymer as well as the pseudoprepolymer, i.e., a mixture of the prepolymer and the polyisocyanate from which the prepolymer is prepared. The isocyanate-

terminated prepolymer useful in the present compositions should have a free isocyanate (NCO) content of from 10 to 29%, preferably 16 to 29%. In general, the polymeric polyisocyanate may be prepared by the reaction of an excess of a polyisocyanate and a polyol, including aminated polyols or imino/enamines thereof.

Suitable polyols for preparing the isocyanate-terminated prepolymers include:

- (a) polyether polyols, thioether polyols and/or hydrocarbon-based polyols having a molecular weight of from 1000 to 6000 and an average hydroxyl functionality of from 1.8 to 4
- (b) polyester polyols having a molecular weight of 1000 or more and an average hydroxyl functionality of from 1.9 to 4.

Particularly preferred isocyanate-terminated prepolymers useful in the present invention are MDI prepolymers, which are the reaction product of an excess of polymeric MDI and polyether polyols. The polyether polyols are preferably diols or triols having hydroxyl values of 25 to 120. The polyol should have a number average molecular weight in the range of 1000 to 6000. Such prepolymers should generally have a free-NCO content of more than 10%, preferably more than 16% and most preferably 16 to 29%. Suitable polymers are those in which the stoichiometric ratio of isocyanate (NCO) to hydroxyl (OH) exceeds 1:1. Rubinate™ M available from ICI Americas is a suitable polymeric MDI composition useful in the present invention.

The second component of the present compositions is an isocyanate-reactive component characterized in that the total ethylene oxide content by weight of the total adhesive composition is more than 2.5%. More preferably, at least 40% of the total ethylene oxide content is present as part of the reactant.

Reactants suitable for the present invention are reactants comprising at least one aliphatic tertiary amine group-containing polyol having an ethylene oxide content of at least 1%.

Preferably, the ethylene oxide content of the reactant is from 1 to 90%, preferably 5 to 60. The aliphatic tertiary amine group-containing polyol provides an ethylene oxide content in the prepolymer of 0.01 to 27%, preferably 0.35 to 12%. Most preferred, the weight ratio of ethylene oxide to propylene oxide in the total composition is at least 1 to 5, said propylene oxide or ethylene oxide being part of the reactant and/or from an additional polyol being present in the total composition.

The aliphatic tertiary amine group-containing polyols are the known alkoxylation products of amines or aminoalcohols with at least two active hydrogen atoms with ethylene oxide and optionally propylene oxide. Suitable initiator molecules include: ammonia, ethylene diamine, hexamethylene diamine, methylamine, diaminodiphenyl methane, aniline, ethanolamine, diethanolamine, N-methyl diethanolamine, and tetrahydroxyl ethyl ethylenediamine.

Suitable aliphatic tertiary amine group-containing polyols are those wherein the initiator comprises 1 to 18 and preferably 1 to 6 carbon atoms. Suitable aliphatic tertiary amine group-containing polyols have an average molecular weight of about 1500 to 10,000 and preferably 1500 to 6000 and an average OH functionality of 1.8 to 6.0.

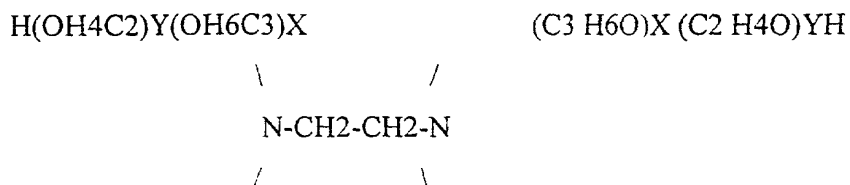
Preferred amine group-containing polyols for use in the present invention includes those prepared from ethylene diamine, triethylene tetramine and triethanolamine.

The present compositions comprise the reactant such as the aliphatic tertiary amine group-containing polyol component, in an amount of 1 to 50%, preferably 7 to 30% and most preferably 10 to 20% by weight based upon the total amount of isocyanate and polyol in the composition.

In its most preferred form, the amine group-containing polyol is an ethylene diamine-based polyol containing ethylene oxide. Suitable ethylene diamine-based polyols are those having an ethylene oxide content of 1 to 90%, preferably 5 to 60%. The ethylene oxide content refers to the amount of ethylene oxide utilized in the preparation of the polyols as discussed above.

During production, the ethylene oxide reacts with the initiator. The polyols should have a molecular weight in the range of 1500 to 6000.

Suitable ethylene diamine-based polyols useful in the present compositions include those of the following formula:



wherein x is an integer of 1.0 to 29.0, preferably 4.0 to 20 and most preferably 4.0 to 14 and y is an integer of 0.1 to 10.0 and preferably 2.0 to 4.0. Suitable ethylene diamine-based polyols are available commercially, such as the "Synperonic T" series of polyols available from ICI Americas Inc.

Preferably, the total ethylene oxide content by weight of the total adhesive composition is more than 2.5%. Most preferred, at least 40% of the total ethylene oxide content is present as part of the reactant. Polypropylene oxide based reactants or additional polypropylene oxide based polyols may be used for the present compositions, preferably whereby the weight ratio of ethylene oxide to propylene oxide is at least 1 to 8, said propylene oxide being part of the reactant and/or from an additional polyol being present in the total composition.

Preferably, the concentration of nitrogen in the amine group-containing polyol is 0.002 to 0.05 eqN/100g.

The said adhesive composition may be produced in any number of ways such as, but not limited to:

- (i) Sequentially mixing the components at temperatures 25-80°C (with the proviso that when using pure MDI it is used above 42°C). Said mixtures are then allowed to react.
- (ii) Sequentially mixing and pre-reacting components (a) and (b).
- (iii) Pre-reacting part of the isocyanate component with one of the isocyanate-reactive components, then separately pre-reacting the rest of the isocyanate component with the other isocyanate-reactive component, and blending the two prepolymers together.

10 Catalysts can additionally be incorporated into the present compositions to further enhance the cure rate of the compositions. Examples of appropriate catalysts are, e.g., tertiary amine catalysts. Suitable tertiary amine catalysts are available commercially, as Niox A-4, from Union Carbide and Thancat DMDEE, from Texaco. Most preferably, the Niox A-4 catalyst is used in the relatively slower cure systems.

15 It has been found however, that reactivity can be controlled by the ethylene oxide in total composition, so limiting the number of formulations which require the addition of extra catalysts.

20 Other additives such as fungicides, tackifiers, UV stabilizers, viscosity reducers, plasticisers, fillers and extenders as well as surface tension modifying agents can be added depending on the specific application or manufacturing procedure. Furthermore, other adhesives such as, but not limited to, UF, PF and PRF can also be incorporated into the formulation.

25 The adhesive compositions of the present invention have been found to have a pot life of approximately three months or more under moisture-free conditions when mixed prior to application to a substrate.

30 The present compositions are also "cold curable", i.e., may be cured at a temperature of 10°C to room temperature although they can also be hot cured. Thus, the present compositions may be cured at temperatures of from 10°C to 250°C. Preferably the present compositions are

cured at a temperature of 23oC to 125oC. Generally, most systems will cure at room temperature in 10-30 minutes.

5 The adhesive compositions of the present invention may be used to bond many different types of moisture-containing substrates. It is preferred that at least one of the substrates be selected from the group consisting of wood, paper, rice hulls, cement, stone, cloth, grass, corn husks, bagasse, nut shells, polymeric foam films and sheets, polymeric foams and fibrous materials. Preferably, the present composition is used to fabricate multi-substrate composites or laminates. Those composites or laminates of particular interest being those comprising
10 lignocellulosic or cellulosic materials, such as wood or paper, to prepare products such as finger joints, "Glulam" and I- Beams, plywood, wafer board, particleboard, fiberboard, chipboard, and oriented wood products, such as "Parallam", available from McMillan Bloedell.

15 As the present adhesive compositions are moisture-activated, it is important that the substrates have relatively high moisture contents. Specifically, the substrates should have moisture contents of at least 7%. Preferably, the substrates have moisture contents of 10 to 20% by weight and more preferably 12 to 15% by weight

20 When used to bond multiple substrates together, the present composition is applied to a surface of a first substrate. A surface of a second substrate is then contacted with the surface of the first substrate containing the present composition. Pressure is then applied to the contacted surfaces and the adhesive compositions are allowed to cure. The surface of the second substrate against which the first substrate is contacted is generally not coated with the present
25 adhesive composition. However, that surface may also be coated prior to contacting the substrates.

The present invention is further directed to a process for bonding multiple substrates comprising

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- (1) applying to a surface of a first substrate the present moisture-activated adhesive composition as defined above and contacting the surface of the first substrate with a surface of a second substrate
- (2) applying pressure to the contacted surfaces, and
- 5 (3) curing the adhesive composition.

Additionally, independent of the moisture content, additional water can be applied to in the following manner

- 10 (a) the first substrate surface prior to the application of the present composition,
- (b) on top of the resin, after application to the first substrate surface and/or
- (c) to the second substrate surface prior to contacting the first, resinated substrate surface, or any combinations thereof, to speed up the reaction

15 Such additions of moisture are called "misting". Misting can optionally be used to increase the accessibility of water to the reactive isocyanate. Preferably, the application levels of water should not exceed 5% of the resin loading.

20 The present adhesive compositions also provide cold tack immediately after application to a substrate. This is particularly useful for pre-press operations where mechanical handling is often necessary. Cold tack is achieved naturally by the present composition adhesives, described in this invention. The present compositions may be used as additives to other resins and adhesives, which require improved tack properties.

25 The present adhesive compositions may be applied to the surfaces of the substrates in any conventional manner. For example, the surface may be coated with the composition by spraying, brushing, etc. Suitable means for applying the adhesive compositions to the surface of the substrate for a particular application will be evident to one skilled in the art from the present disclosure.

After the coated substrates are contacted with each other, pressure is applied thereto. The pressure should be sufficient to cause the surfaces to adhere to one another. Generally, the amount of pressure and the time period for which the pressure is applied are not limited and specific pressures and times will be evident to one skilled in the art from the present disclosure. However, it has been found preferable that a pressure of approximately 10 to 200 psi (equivalent to 69 to 1380 kPa) be applied for 10 to 20 minutes to cause appropriate adhesion for most substrates. Further processing can generally be conducted on the treated substrates in less than one hour.

The invention is now illustrated by the following examples, which are not intended to limit the scope of the invention.

EXAMPLES

The following adhesive compositions were prepared in accordance with the present invention.

Example 1

	MDI prepolymer	80
	Polyol 1	20

The MDI prepolymer had an NCO content of 24.9% and was prepared by reacting Rubinol F-456 (a polyether diol available from ICI Americas Inc.) with a 69/31 blend of polymeric MDI to pure MDI. The polymeric MDI used was Rubinate™ M and the pure MDI used was Rubinate™ 44, both available from ICI America Inc. Polyol 1 was "Synperonic T 304" which is an ethylene diamine-based polyol available from ICI Americas Inc.

Total EO % by weight of the total adhesive composition is 8%.

Comparison example 2a

	MDI prepolymer	80
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Polyol 2

20

The MDI prepolymer had an NCO content of 24.9% and was prepared by reacting Rubinol F-456 (a polyether diol available from ICI Americas Inc.) with a 69/31 blend of polymeric MDI to pure MDI. The polymeric MDI used was Rubinate™ M and the pure MDI used was Rubinate™ 44, both available from ICI Americas Inc. Polyol 2 was "Synperonic T 701" which is an ethylene diamine-based polyol available from ICI Americas Inc.

Total EO % by weight of the total adhesive composition is 2.2%.

10 Example 2b

MDI prepolymer	63.58
Polyol 2	1.91
Polyol 1	8.27
Niax A-4	0.64
Calcium Carbonate No.7	25.43
SAG 47	0.07

Same as example 2a with SAG 47 is an antifoam agent available from Union Carbide. NiaxA-4 is a suitable tertiary amine catalysts available from Union Carbide.

Total EO % by weight of the total adhesive composition is 1.6%.

Example 3

MDI prepolymer	84.4
Polyol 1	15.05
DMDEE	0.05

The MDI prepolymer had an NCO content of 25.2% and was prepared by reacting Rubinol F-456 (a polyether diol available from ICI Americas Inc.) with a 71.2/28.8 blend of polymeric MDI to pure MDI. The polymeric MDI used was Rubinate™ M and the pure MDI used was

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Rubinate™ 44, both available from ICI Americas Inc. Polyol 1 was "Synperonic T 304" which is an ethylene diamine - based polyol available from ICI Americas Inc.

Total EO % by weight of the total adhesive composition is 6%.

5 Example 4

MDI prepolymer	80
Polyol 1	20

- 10 The MDI prepolymer had an NCO content of 24.9% and was prepared by reacting Rubinol F-481 (a polyether diol available from ICI Americas Inc.) with a 69/31 blend of polymeric MDI to pure MDI. The polymeric MDI used was Rubinate™ M and the pure MDI used was Rubinate™ 44, both available from ICI Americas Inc. Polyol 1 was "Synperonic T 304" which is an ethylene diamine - based polyol available from ICI Americas Inc.
- 15 Total EO % by weight of the total adhesive composition is 12%.

Example 5

	Polymeric MDI	45
20	44 MDI	20
	Rubinol F456	15
	Synperonic T 304	20

- The products were made by sequential addition of the different components. The final NCO, viscosity and properties are the same as in Example 1.
- 25

Total EO % by weight of the total adhesive composition is 8%.

Results :

- 30 Reactivity test measured as the time taken to start foaming when formulation is contacted on a 10% moisture containing aspen wood showed that the formulation

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according to example 1 and 4 is significantly faster than formulation of example 2 and equivalent to the formulation of example 3 (formulation with catalyst).

Formulations given in examples 1 and 4, were used to construct single lap joints using 150 x 25 x 3 mm tangentially cut aspen wood. Overlaps were 25 x 25 mm and resin loadings were 12 mg.m⁻². The lap joints were cured at room temperature for 15 minutes and tested to failure. Two sets of samples were produced. In the first instance, the resin was applied to the wood of moisture content 10%. In the second case, after the application of the adhesive, an additional 5% (based on adhesive weight), water content was applied by spray onto the adhesive layer. The loads to failure were recorded. The results, listed below, show a much higher tensile shear strength and higher percentages of wood failure for the systems with added water.

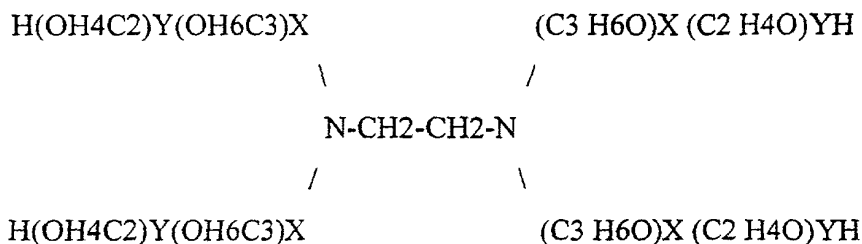
Tensile Strength failure loads in MPa

	Without mist	With mist
Example 1	0.6	3.5
Example 5	0.6	3.5

CLAIMS

1. A moisture-activated adhesive composition comprising the reaction product of
- 5 (A) a polyisocyanate selected from (a) a blend of polymeric MDI and pure MDI and/or from (b) an isocyanate-terminated prepolymer.
- (B) an isocyanate-reactive component comprising at least one aliphatic tertiary amine group-containing polyol made by alkoxylation of amines or aminoalcohols
- 10 characterized in that the total ethylene oxide content by weight of the total adhesive composition is more than 2.5%
- 2 A moisture-activated adhesive composition according to claim 1 whereby at least 40% of the total ethylene oxide content is present as part of the reactant
- 15 3. A moisture-activated adhesive composition according to claims 1-2 whereby the weight ratio of ethylene oxide to propylene oxide is at least 1 to 8, said propylene oxide being part of the reactant and/or from an additional polyol being present in the composition
- 20 4. A moisture -activated adhesive composition according to claims 1-3 whereby the total nitrogen concentration of the total composition is from 0.002 to 0.05 eqN/100 g
- 25 5. A moisture-activated adhesive composition according to claims 1-4, wherein said polymeric polyisocyanate is a polymeric diphenylmethane diisocyanate.
6. A moisture-activated adhesive composition according to claim 1-5, wherein said isocyanate-terminated prepolymer having an NCO content of 10 to 29 %.
- 30

7. A moisture-activated adhesive composition according to claim 6, wherein said isocyanate-terminated prepolymer is the reaction product of polymeric diphenylmethane diisocyanate and a polyether polyol having a molecular weight of from 1000 to 6000.
8. A moisture-activated adhesive composition according to claim 1, wherein said reactant is an aliphatic tertiary amine group-containing polyol having an ethylene oxide content of 1 to 90 %.
9. A moisture-activated adhesive composition according to claim 8, wherein said aliphatic tertiary amine group-containing polyol has an ethylene oxide content of 5 to 60 %.
10. A moisture-activated adhesive composition according to claim 1, wherein said aliphatic tertiary amine group-containing polyol has a molecular weight of 1500 to 10,000 and comprises an initiator having 1 to 18 carbon atoms.
11. A moisture-activated adhesive composition according to claim 1, wherein said aliphatic tertiary amine group-containing polyol is prepared from a compound selected from the group consisting of ethylene diamine, triethylene tetramine and triethanolamine.
12. A moisture-activated adhesive composition according to claim 11, wherein said aliphatic tertiary amine group-containing polyol is an ethylene diamine-based polyol having the following formula:



wherein x is an integer of 1 to 29.0 and y is an integer of 0.1 to 10.

13. A moisture-activated adhesive composition according to claim 1, further comprising a catalyst.

14. A process for bonding multiple substrates comprising

(1) applying to a surface of a first substrate a moisture-activated adhesive composition as defined in any one of the preceding claims

(2) contacting said surface with a surface of a second substrate

(3) applying pressure to the contacted surfaces, and

(4) curing said adhesive composition.

15. A process according to claim 14, wherein said substrate has a moisture content of at least 7 % by weight.

16. An engineered lumber product prepared by the process according to claim 14.

17. A process for bonding according to claim 16, wherein additional moisture is applied to the first substrate surface, the surface of the applied adhesive and/or the surface.

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DECLARATIONS

RULE 63 (37 C.F.R. 1.63)
DECLARATION AND POWER OF ATTORNEY
FOR PATENT APPLICATION
IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

PW
FORM

As a below named inventor, I hereby declare that my residence, post office address and citizenship are as stated below next to my name, and I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the INVENTION ENTITLED Moisture-activated adhesive compositions

the specification of which (CHECK applicable BOX(ES))
X A. ☐ is attached hereto.
BOX(ES) → B. ☐ was filed on _____ as U.S. Application No. _____ /
→ C. ☒ was filed as PCT International Application No. PCT/ EP00/00034 on 05 January 2000
and (if applicable to U.S. or PCT application) was amended on _____

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above. I acknowledge the duty to disclose all information known to me to be material to patentability as defined in 37 C.F.R. 1.56. Except as noted below, I hereby claim foreign priority benefits under 35 U.S.C. 119(a)-(d) or 365(b) of any foreign application(s) for patent or inventor's certificate, or 365(a) of any PCT International Application which designated at least one other country than the United States, listed below and have also identified below any foreign application for patent or inventor's certificate, or PCT International Application, filed by me or my assignee disclosing the subject matter claimed in this application and having a filing date (1) before that of the application on which priority is claimed, or (2) if no priority claimed, before the filing date of this application:

PRIOR FOREIGN APPLICATION(S)	Date first Laid-	Date Patented	Priority NOT Claimed
Number	open or Published	or Granted	

If more prior foreign applications, X box at bottom and continue on attached page.

Except as noted below, I hereby claim domestic priority benefit under 35 U.S.C. 119(e) or 120 and/or 365(c) of the indicated United States applications listed below and PCT international applications listed above or below and, if this is a continuation-in-part (CIP) application, insofar as the subject matter disclosed and claimed in this application is in addition to that disclosed in such prior applications, I acknowledge the duty to disclose all information known to me to be material to patentability as defined in 37 C.F.R. 1.56 which became available between the filing date of each such prior application and the national or PCT international filing date of this application:

PRIOR U.S. PROVISIONAL, NONPROVISIONAL AND/OR PCT APPLICATION(S)	Status	Priority NOT Claimed
Application No. (series code/serial no.)	Day/MONTH/Year Filed	pending, abandoned, patented
60/117417	27 January 1999	A

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

And I hereby appoint Pillsbury Winthrop LLP, Intellectual Property Group, telephone number (703) 905-2000 (to whom all communications are to be directed), and persons of that firm who are associated with USPTO Customer No. 909 (see below label) individually and collectively my attorneys to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith and with the resulting patent, and I hereby authorize them to delete from that Customer No. names of persons no longer with their firm, to add new persons of their firm to that Customer No., and to act and rely on instructions from and communicate directly with the person/assignee/attorney/firm/ organization who/which first sends/sent this case to them and by whom/which I hereby declare that I have consented after full disclosure to be represented unless/until I instruct the above Firm and/or an attorney of that Firm in writing to the contrary.

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☒ FOR ADDITIONAL INVENTORS see attached page.
☐ See additional foreign priorities on attached page (incorporated herein by reference).

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Mailing Address			
(include Zip Code)			